Date: January 24, 2006

To: Jim Anderson, DEQ NWR, Manager, Portland Harbor Section

From: Jennifer Peterson, DEQ NWR, Toxicologist, Portland Harbor Section with incorporated comments from Bruce Hope, DEQ Headquarters, Air Quality, Toxicologist

RE: Food Web Modeling Report: Evaluating TrophicTrace and the Arnot and Gobas Models for Application to the Portland Harbor Superfund Site, DRAFT, November 4, 2005, Prepared for The Lower Willamette Group by Windward Environmental

General Comments:

1. Graphs, charts, and figures should be included to explicitly show what food webs are modeled.

2. DEQ has completed a general review of the food web model parameters and structure. Additional comments and clarification will follow when a working copy of the Arnot and Gobas model can be completed. This is needed to complete the review.

3. In general, averages are prevalent in these modeling efforts in both time and space. This can obscure variability and heterogeneity, which may result in high model accuracy while hiding relevant ties to those processes which control bioaccumulation, such as organism exposure and environmental parameters. Averaging across the entire the harbor will also obscure the location of specific contaminant loads. Future runs should compare instantaneous measurements with instantaneous model results where possible.

4. We can agree that Arnot & Gobas is the suitable food web model for Portland Harbor and thus there is no need for further comparisons with other models. Being able to focus on just one model should free-up time to improve the efficiency of the sensitivity and uncertainty analysis processes, parameterization, and to begin developing a transport and fate model to accompany the food web model. Currently, mostly general comments are provided on the food web model. Detailed comments on the LWG's parameterization of the model require runs of the model, which has not yet been completed by the government team.

5. Direction on linked food web and transport and fate elements: These are directed answers to some of the basic questions that will need to be addressed during development of the Portland Harbor transport and fate (T&F) and food web models.

Model Purpose

1. Provide managers with information about possible long-term outcomes from various remediation options
2. Provide estimates of residue levels in species (e.g., sturgeon, great blue heron) for which empirical data are unlikely to be available.
3. Because so much empirical data will be available to support the ecological risk assessment, there may be little need for the model here

Model Elements

- A simple mass balance T&F model linked to food web models will be required. Such a linkage has been accomplished elsewhere.[1]
- The T&F model can be developed from several variations available in the literature, all of which have proven useful in situations similar to Portland Harbor.[2, 3]
- The food web models should be based on the form initially established by Gobas and subsequently improved by him and others.[4]
- To address the issue of receptor exposures while moving (foraging), divide the harbor into segments within the T&F model (see below), develop a similar food web model for each segment, and apportion exposure to a mobile receptor as a function of its estimated residence time in each segment.

Temporal Granularity & Scale

- The models must be dynamic (time-dependent) so that it is possible to track changes over time (in response to possible remedial alternatives) and to determine how long it will take the system to approach steady-state.[5]
- Steady-state only models are not acceptable.
- Both models will need to incorporate seasonally varying data (e.g., river flow rate, water temperature, etc.). A monthly period will provide a reasonable balance between model resolution and the amount of data generated.

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1 Mackay D, Sang S, Vlahos P, Diamond M, Gobas F and Dolan D. 1994. A rate constant model of chemical dynamics in a lake ecosystem: PCBs in Lake Ontario. Journal of Great Lakes Research 20(4): 625-642.

2 Davis JA. 2003. The long term fate of PCBs in San Francisco Bay. RMP Technical Report: SFEI Contribution 47. San Francisco Estuary Institute, Oakland, CA.

3 Davis JA. 2004. The long term fate of PCBs in San Francisco Bay. Environmental Toxicology and Chemistry 23(10): 2396-2409.

4 Arnot JA and Gobas FAPC. 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environmental Toxicology and Chemistry 23(10): 2343-2355.

5 Mackay D. 2001. Multimedia Environmental Models: The Fugacity Approach, Second Edition. 2001. Lewis Publishers, Boca Raton, FL. p.212.

- The time increment (*dt*) must be sufficiently small to capture changes which occur within the course of a time unit (i.e., a month).
- Because of the half-life of some of the contaminants involved, the model should be capable of estimating forward 20-25 years, on a monthly basis.

Spatial Granularity & Scale

- A multi-segment model is required.[6, 7]
- The model domain should extend from river mile (RM) 11 to RM 2, with a separate compartment for Swan Island Lagoon.
- This domain should be divided into segments, both horizontally and longitudinally, on the basis of appropriate physical parameters.
- Other segmentation patterns (parallel to flow, by habitat, etc.) may be considered after the basic T&F model is built.

Flow Regimes

- USGS data are available from RM 12.8 to provide measures of flow on a daily basis for 30+ years.
- During the summer low flow period, flow reversals and intrusion of Columbia River water can occur. The T&F model should be able to accommodate these phenomena at least to the point where there impact on contaminant movement can be assessed.

Loadings

- The T&F model should make provision loads that enter Segment 1 from upstream sources (those above RM 11).
- The T&F model should also make provision for including loadings from various sources (e.g., overland, outfalls, groundwater, etc.), even if the quantities of loadings from such sources are currently unknown.

Contaminants

- Polychlorinated biphenyls. As there are numerous congeners, it may be expedient to use PCB 118 as a surrogate for this group.[8]
- Polycyclic aromatic hydrocarbons. Again, another large group - a subset will need to be identified for modeling, as was done for San Francisco Bay.[9, 10] It appears that the metabolism of these

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[6] See Mackay (2001), p. 210.

[7] Mackay D and Hickie B. 2000. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. Chemosphere 41: 681-692.

[8] See Davis (2003, 2004).

[9] Greenfield BK and Davis JA. 2004. A simple mass balance model for PAH fate in the San Francisco Estuary. RMP Technical Report, SFEI Contribution 115. San Francisco Estuary Institute, Oakland, CA.

[10] Greenfield BK and Davis JA. 2005. A PAH fate model for San Francisco Bay. Chemosphere 60: 515-530.

contaminants by some aquatic species can be addressed within the type of food web model contemplated here.[11]

- Pesticides, represented by DDE, since it is the more toxic, persistent, and bioaccumulative of by-product of DDT. Using ΣDDT is not recommended as this can obscure important physicochemical differences among DDT, DDE, and DDD.
- These models are not designed to address metals mechanistically. Metals that are actually expected to biomagnify may be only secondary concern.[12] Modelling methylmercury would require a different, specialized, model, which may not be justified at this time.

Food Web Complexity

- The Arnot and Gobas formulation of the Gobas food web model is preferred.[13, 14]
- An overly detailed food web, with numerous species, is likely to exceed both the availability of site-specific data (i.e., data from 6 fish aren't enough), as well as literature-derived physiological data.
- As the models' primary purpose is to inform remediation decisions and not precisely predict tissue residues, a simplified food web, encompassing representative pelagic and benthic species, should be sufficient at this time.
- A food web model in each segment will address the issue of receptor range and movement.
- Using matrix methods, it is possible to include scavenging and/or cannibalism feeding behaviors in these food webs.[15] However, to minimize model complexity, these feeding relationships should be excluded unless there is a compelling reason to do otherwise.
- Fluctuations in dietary preference can be addressed by normalizing dietary fractions across a "menu" of possible food items.[16]

Data Availability

11 **Stevenson RW. 2003. Development and application of a model describing the bioaccumulation and metabolism of polycyclic aromatic hydrocarbons in a marine benthic food web. M.S. thesis, School of Resource and Environmental Management, Simon Fraser University, British Columbia, Canada.**

12 **Reinfelder JR, Fisher NS, Luoma SN, Nichols JW and Wang WX. 1998. Trace element trophic transfer in aquatic organisms: a critique of the kinetic model approach. Science of the Total Environment 219(2-3): 117-135.**

13 **See #4.**

14 **Gobas F and Wilcockson J. 2003. San Francisco Bay PCB food-web model. RMP Technical Report, SFEI Contribution 90. San Francisco Estuary Institute, Oakland, CA.**

15 **Sharpe S and Mackay D. A framework for evaluating bioaccumulation in food webs. Environmental Science & Technology 34(12): 2373-2379.**

16 **USEPA. 2003. Multimedia, Multipathway, and Multireceptor Risk Assessment (3MRA) Modeling System. Volume I: Modeling System and Science. EPA 530-D-03-001a. Office of Research and Development / Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC. Section 12, page 12-8.**

- The initial goal is a set of integrated working models that capture the principle features of abiotic and biotic T&F within the harbor. Achieving working models should not be held hostage to data availability.
- The models should therefore be initially built-out with available site-specific data and appropriate data from the literature. Data gaps should be both identified and filled with information based on best professional judgment. Placeholders should be left for key items (e.g., loadings) which are already known to be important but may not be quantified for some time.
- Sensitivity analysis should be used to narrow our interest in data gaps to those which have the greatest impact on model performance.
- These data gaps can then be addressed in greater detail as the models progress through various editions and refinements.

Model Platform

- **The key determinant of which platform (i.e., software) to use is transparency, which is defined as the ability for an informed user to follow (if desired) every step of model operation. "Black box" approaches are to be minimized, if not simply avoided.**
- **The models should be written in an accessible program like VBA™, with input/output through Excel™ spreadsheets, with "elegant" or otherwise "streamlined" coding being discouraged in favor of transparency.**
- **The one area where some transparency may be sacrificed is with respect to analysis of uncertainty and sensitivity. For these, use of a Monte Carlo software (e.g., CrystalBall®, @Risk®, etc.) capable of linking to both Excel™ spreadsheets and VBA™ should be considered. This would considerably simplify the currently cumbersome approach to both of these analyses.**

Specific Comments:

Page ES-1, Last Paragraph: It is unclear what additional new tools for summarizing sediment chemistry data will be used for future modeling.

Page ES-2, 2nd para. The model should not be used to generate preliminary remedial goals.

Page 3, bullet 7. The need for a T&F model should not be interpreted as something that does not have to be accomplished along with the food web model. The availability of a T&F model should not be left open, but should go along with the food web model.

Page 5, Section 2.1.2, Abiotic Media: It is unclear why total dissolved and particulate concentrations were used in the model (e.g. for surface water) when the individual measurements of both were analyzed for in Portland Harbor sampling.

Page 6, Section 2.2.2, Aqueous Uptake: While it is an important exposure route to consider for invertebrates, it is unclear why ventilation of porewater for fish was included in the Arnot and Gobas model. It is unlikely that any fish would be ventilating porewater at the site, with the *possible* exception of sculpin. Even so, it would likely be a transition zone water exposure.

Page 8, reference to Table 3-1. This table does list most of the equations used in the Arnot & Gobas model. However, the model as implemented in the template does not necessarily follow exactly the model described in the literature. For example, the table fails to note that one version of the model uses fugacity concepts to arrive at the final tissue residue estimate and in certain instances (e.g., VLG, VNG, VWG) the table's concise format fails to convey that the results are arrived at as sums of products (e.g., Excel SUMPRODUCT). This indicates that more needs to be done to fulfill the transparency specification, in that each and every equation, parameter, and value used in the actual model must be fully and transparently documented, with more than just a summary table.

Page 9, Section 3.3. ECOFATE was offered only as an example of the type of integrated transport & fate / food web model desired for Portland Harbor. We acknowledge that it is somewhat dated and has limitations. However, its existence (and that of similar models) indicates that such an integrated approach is possible, has been found useful in similar river systems, and could therefore be implemented for Portland Harbor. The absence of loadings data is not a valid reason for rejecting the development and use of such an integrated model, as such information can be estimated with the model and then checked in the field.

Page 12, Section 4.1.2. An average over the entire site (RM2-11) is not useful as this approach may easily obscure significant changes occurring over short distances or localized impacts associated with specific sources. Smaller, biologically-defined scales (such as those associated with different fish species) can be accommodated by creating copies of the model at these smaller scales and then pro-rating the results over the scale of each species.

Page 14, 1st Paragraph: It is unclear why the model was altered to accept species-specific porewater ventilation rates for fish expected to be primarily water column feeders, such as black crappie. This scenario may be only appropriate to apply to true benthic fish, such as sculpin. Arnot and Gobas only have crayfish and other invertebrates ventilating porewater, at a generic 5% value. Table 4-3 has the following: 0.2 crayfish, brown bullhead .005, carp .08, black crappie .005, sculpin .02, sucker .08, and juvenile fish 0.01 – all based on best professional judgment. In the absence of additional information, Arnot and Gobas recommendations should be followed.

Page 14, last para. The Arnot & Gobas model is able to model two basic feeding guilds of benthic invertebrates - filter feeders & detritivores / scavengers - but not necessarily specific species.

Page 15, Section 4.4. A graphic or diagram of the various food webs would be helpful (if this is Figure 2-1, then connections should be shown other than with different colors which do not copy). Because the model is ultimately intended for somewhat generic (FS and planning) purposes, it may be sufficient to use a representative, but simplified, food web throughout the site. It would be more explicit to the reader / reviewer to use one food web structure and use uncertainty analysis (e.g. Monte Carlo variables) to represent variability in dietary fractions for each species. Running multiple model runs with differing dietary fractions in order to conduct uncertainty and sensitivity analysis is cumbersome and difficult to review. All scenarios can't be run, leading to uncertainty in terms of the importance of the dietary fraction on the results.

Page 17, Section 4.2.1.2, Environmental Parameters: Why is a MDEQ 2004 document referenced for determining sediment and surface water concentrations from Round 1 and 2 sampling events?

Empirically measured data on environmental parameters should be used over modeled data (e.g. for dissolved oxygen). It is unclear why measurements of TOC, total suspended solids (TSS) and temperature were taken from the ODEQ LASAR database, but not dissolved oxygen data. If available, co-collected TSS and concentration data should be used (isn't TSS data available from the surface water sampling events?).

Page 17, Section 4.2.1.2, Environmental Parameters, Sediment Chemistry: How was SOC calculated?
We should be able to review and understand how the area-weighted average was calculated here. The methodology to for calculating these values is not presented in this report, and cannot be replicated. However, perhaps the bigger comment is that we do not feel that averaging over large distances is applicable for this modeling effort. Also, it may not be appropriate to use an average concentration that includes the channel of the river for some species (e.g. smallmouth bass; sculpin) that do not likely inhabit that area. I may be better to model the shorelines only for some species.

Page 18, Section 4.2.1.2, Environmental Parameters, Water Chemistry: Only total chemical concentrations were used in the model (sum of concentrations from the XAD filter and water column). In the absence of empirical data on dissolved and particulate concentrations, the model calculates these fractions. However, since empirical data does exist from the XAD analysis, these data should be used in model. The Arnot and Gobas model parameters are: chemical concentration in water (total) and chemical concentration in water (dissolved).

Page 19, Section 4.2.1.2, Environmental Parameters, Water Chemistry: Despite the existence of XAD data in Swan Island Lagoon, surface water data averaged over the entire site was used for the Swan Island model runs (small spatial scale)(see also page 31, Section 5.1.1.2). Site-specific water data from Swan Island should be used in the model runs, especially given the sensitivity to water data in the model. It is not necessary to have a spatially averaged water sample before it is included in the model.

Page 19, Section 4.2.1.2, Environmental Parameters, Water Chemistry: The text states here that DO, temperature and TSS were calculated from the LASAR database. It should be mentioned here that the DO values were not used in the model (they were calculated using an Arnot and Gobas equation), as indicated on page 17.

Page 19, Section 4.2.1.3, Chemical Parameters: It seems like for initial modeling purposes we should be assuming all DDT is DDE (if DDT is detected in tissue it will be metabolized to DDE), and that DDE is not metabolized (or very little). I wouldn't say that the conversion of DDT to DDE would balance out the metabolism of DDE, since this is very slow.

Page 20, Section 4.2.2.1, Trophic Trace Biological Parameters: Why are insect larvae, such as chironomids, and crayfish selected for the "water pathway"? These are primarily in direct contact with the sediment. In the case of crayfish, the primary exposure route should be selected, regardless of the existence of a relationship between sediment and tissue (e.g. this could be for other reasons).

Page 21, Section 4.2.2.3, Chemical Parameters: Where did the literature value used for the BSAF fall in the range of site-specific BSAFs (e.g. that ranged over 3 orders of magnitude?).

Page 22, Section 4.2, Model Evaluation Methods: Arnot and Gobas (2004) present an evaluation of model performance bias in order to evaluate various modifications to model revisions between the 2004 model and the 1993 model. Model bias is mentioned here, as it is in the Arnot and Gobas publications. However, it is unclear what the basis of the three other model criteria; the species predictive accuracy factor (SPAF), model predictive accuracy factor (MPAF) and the percentage change. We should agree on the criteria used for evaluating the predictive power of the models before the next iteration of the model. [I don't understand these criteria at present, but some of them don't seem appropriate. The bigger comment still remains that evaluating averages over the site are not relevant, but perhaps Bruce will have some ideas after he gets the model up and running.

Page 25, Section 4.5.1. The sensitivity analysis is valuable but could have been done more efficiently with software intended for this purpose. It would have been vastly more efficient, with respect to both the sensitivity and uncertainty analyses, to run the model with some type of Monte Carlo software. This may not have been possible because TrophicTrace is a "black box" (i.e., not an open spreadsheet). However, focusing on the Arnot & Gobas model, which is an accessible spreadsheet, should allow more efficient sensitivity analysis methods to be used.

Page 27, Section 4.5.2. As an uncertainty analysis, this approach seems flawed and not much more than an additional sensitivity analysis. The random selection of a value from within a range of plausible values, where the probability of selection is defined by some distribution, with consideration (when appropriate) for correlation among variables, does not appear to be a factor here. Instead, variables were moved to high or low values as a group, without randomness or regard for potential correlations. Thus, for example, water temperature and TSS are both high simultaneously whereas we know the opposite is true - higher summer temperatures coincide with low flows that support lower TSS values. As noted before, focusing on just one model should allow for an actual uncertainty analysis to be performed.

Page 28, Section 4.5.2.2, 4,4'DDE: Given that DDT is present at the site and in tissue, metabolism of DDT to DDE needs to be represented in the model. The easiest way is to assume measured DDT concentrations are DDE (in tissue this is always the case). The text mentions this, and then states conversion factors of 20, 50 or 100% DDT were added to the DDE values. However, it is unclear if this analysis was done. The results are not discussed on page 31, section 5.1.3 last paragraph, page 22, Section 4,4'-DDE Kow, or page 42, section 5.2.1.3, where these results could have been discussed. In fact, some of the text indicates that the conversion process was excluded.

Page 32, Section 5.1.1.4, 4,4'DDE: If the model is predicting clam issue poorly, then why weren't the clam samples from the site used?

Page 25, Section 5.1.2.1, Highly Sensitive Parameters, Percent Moisture and Lipid: Given that percent moisture is a highly sensitive parameter, uncertainty needs to be reduced by using site specific values and ranges for each species.

Page 52, Section 5.3, 1st Paragraph, Surface characterization of Contaminants: The definition and characterization of surface sediment concentrations has been shown to be important in adequately modeling contaminant uptake. This active zone is likely to be less than 30 cm. The fact that congener data was used for surface water, and Aroclor data was used for sediment and tissue may also lead to some inconsistencies in concentrations –

were different analysis used (e.g. Axys versus EPA CAS method 8081)? If so, is there some bias we need to account for? Can we try congener data only for sediment, tissue and water (even though the data may be more limited)?

Page 52, Section 5.3, 2nd Paragraph, Cannibalism considerations: Arnot and Gobas describe a method by which scavenging and/or cannibalism can be used in model equations using a matrix solution (Campfens and Mackay, 1997).

Page 52, Section 5.3, Juvenile Compartment: It is unclear why the juvenile compartment created here included peamouth and black crappie, which juveniles of these species were not collected.

Page 57, Section 6.2, Filling Data Gaps: It is unclear what additional new tools for summarizing sediment chemistry data will be used for future modeling.

Page 58, Section 6.2, Time Weighted Averages: The model should be able to run under different conditions (e.g. different water collection efforts). Time weighted averages should not be used.

Page 60, Section 6.3.2, Estimating Time to Recovery: A time varying model is needed to meet this objective with the appropriate amount of certainty. See general comment.

Page 61, Section 6.3.3, Modeling Other Chemicals: The models can be run with PAHs, with the use of a metabolism factor.

Figure 2-1, Dietary and Aquatic Chemical Exposure Pathways:
Crayfish: Their diet should include some sediment and detritus. Scavenging?
Black Crappie: This species diet should consist mostly of zooplanton (e.g. see Arnot and Gobas supplementary archive – they have it at 75%). This may be one reason why the model is not predicting tissue concentrations adequately.

<u>Table 3-1, Arnot and Gobas Model: Equations:</u>
Freely Dissolved Chemical Concentration in Porewater: What is the source for this equation? Why is the conc. in sediment multiplied by the density of organic carbon?
Bioavailable Solute Fraction: Data exists on particulate concentrations in the water.
Freely Dissolved Chemical Concentration in Surface Water: Dissolved measurements were collected and should be used instead of the equation.
Freely Dissolved Oxygen Conc. of Water: Empirical measurements exist and should be used in the modeling runs instead of the equation. See also page 19.
<u>Koc:</u> Why was this equation used to calculate Koc? TrophicTrace uses LogKoc = 0.00028 = 0.983 x LogKow.

Table 4-1, Arnot and Gobas, Site Specific Information:
Please see general comment on the use of averages, however, if spatially weighted averages and inverse distance weighting are to be used at any scale, the methodology must be presented and reproducible.

Sediment organic carbon: It is unclear why the values of 1.84 and 2.02 were selected for the ISA and Swan Island Lagoon (e.g. Swan Island value was 2.02 when the mean was 1.86 and the geo mean was 1.42).

Dissolved / Total Water Concentrations: Use site-specific water concentrations.

Disequilibrium Factors: Why is a disequilibrium factor of 1 being used for DOC and POC? A disequilibrium factor of 1 would indicate we have evidence that conditions are at equilibrium. Disequilibria between organic carbon and water have been observed for a range or organic chemicals, including PCBs (Arnot and Gobas 2004).

Table 4-3:

Diet, all species: See previous comment on diet. We should agree on general representatives for the diet and assume all species can consume from the "representatives" varying amounts. Monte Carlo analysis can be used to interpret the results in terms of uncertainty and sensitivity in diet composition. This will be much easier to interpret. Ranges for parameters such as lipid content, moisture content, and weight should also be used in future model runs.

Phytoplankton and Zooplankton: Lipid content; non-lipid content, moisture content: In absence of good relevant freshwater values, we should stick with the literature from the Arnot and Gobas model (2004, Supplementary Archive) that references values from Lake Ontario, Lake Erie, and Lake St. Clair. Values listed here for phytoplankton are from the Burrard Inlet in Vancouver BC, a saltwater system, and have low reported lipid and NLOM values compared to the Arnot and Gobas values. For zooplankton the referenced values are also for marine organisms from a variety of different sources. A non-lipid organic matter value should be used for zooplankton as well (Arnot and Gobas reports 20%).

Clam, Crayfish, Insect Larvae, Oligochaete and Fish: Why weren't NLOM values used for these species? Arnot and Gobas demonstrated that "the inclusion of NLOM and water content organism composition fractions as potential storage sites for organic chemicals in fish results in modest increases in the chemical concentrations in fish and subsequent reductions in model error." It would be especially important to use NLOM for organism with low lipid content such as phytoplankton, algae, and invertebrates.

<u>Table 4-4, TrophicTrace Model:</u> I didn't review since we seem to agree to go with the Arnot and Gobas model. However, some of the same comments apply. Site Use Factor: What was the site use factor in TrophicTrace for the Swan Island Lagoon?

<u>Table 4-6 to 5-4:</u> I didn't review.